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(54) PRODUCTION OF CATALYST FOR PURIFYING EXHAUST GAS

(57)Abstract:

PURPOSE: To improve purification performance of NOx in the lean atmosphere by allowing a monolithic carrier to be spread with slurry in which zeolite, silica sol, alumina sol and water are blended and calcining it and thereafter immersing it in a metallic salt aq. soln.

CONSTITUTION: Slurry is prepared by mixing zeolite, silica sol, alumina sol and water. A monolithic carrier is spread with this slurry and thereafter calcined to form a catalyst carrier. Then a catalyst for purifying exhaust gas is produced by immersing this catalyst carrier in a metallic salt aq. soln. of metal utilized as the catalyst and allowing zeolite to be carried with the metal utilized as the catalyst by ion exchange. A mixing ratio of silica sol and alumina sol is preferably regulated to such mixing ratio that Si/Al thereof is not made far from Si/Al of zeolite.

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TITLE: PRODUCTION OF CATALYST FOR PURIFYING EXHAUST GAS

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CONSTITUTION: Slurry is prepared by mixing zeolite, silica sol, alumina sol and water. A monolithic carrier is spread with this slurry and thereafter calcined to form a catalyst carrier. Then a catalyst for purifying exhaust gas is produced by immersing this catalyst carrier in a metallic salt aq. soln. of metal utilized as the catalyst and allowing zeolite to be carried with the metal utilized as the catalyst by ion exchange. A mixing ratio of silica sol and alumina sol is preferably regulated to such mixing ratio that Si/Al thereof is not made far from Si/Al of zeolite.

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④発明の名称 排気ガス浄化用触媒の製造方法

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明細書

範囲第1項記載の方法。

1 発明の名称

排気ガス浄化用触媒の製造方法

2 特許請求の範囲

1) 以下の工程:

- (a) ゼオライト、シリカゾル、アルミナゾル及び水を混合してスラリーを調製する工程、
 - (b) 上記スラリーを一体型担体に付着させ、焼成する工程、
 - (c) 触媒用金属の金属塩水溶液に浸漬してゼオライトに触媒用金属をイオン交換する工程
- からなることを特徴とする排気ガス浄化用触媒の製造方法。

- 2) シリカゾルとアミルナゾルの混合比は、それらのSi/Al比がゼオライトのSi/Al比にほど遠くはならない混合比であることを特徴とする特許請求の範囲第1項記載の方法。

- 3) 工程(c)は、工程(a)及び(b)よりも後で行なわれる工程であることを特徴とする特許請求の

3 発明の詳細な説明

<産業上の利用分野>

本発明は自動車の排気ガス浄化用触媒、特に空燃比が、リーン側となる酸素過剰空気においてもNO_xを高率に浄化できる触媒の製造方法に関するものである。

<従来の技術>

自動車の排気ガス浄化用触媒として、一酸化炭素(CO)及び炭化水素(HC)の酸化と、窒素酸化物(NO_x)の還元を同時にを行う触媒が汎用されている。このような触媒は、例えば特公昭58-20307号公報にもみられるように、耐火性担体上のアルミニコート層に、Pd, Pt, Rh等の貴金属、及び場合により助触媒成分としてCe, La等の希土類金属又はNi等のベースメタル酸化物を添加したものが殆んどである。

かかる触媒は、エンジンの設定空燃比によつて浄化特性が大きく左右され、希薄混合気つまり空燃比が大きいリーン側では燃焼後も酸素(O₂)

の量が多くなり、酸化作用が活発に、還元作用が不活発になる。この逆に、空燃比の小さいリーン側では酸化作用が不活発に、還元作用が活発になる。この酸化と還元のバランスがとれる理論空燃比 ($A/F = 14.6$) 付近で触媒は最も有効に働く。

従って、触媒を用いる排気ガス浄化装置を取付けた自動車では、排気系の酸素濃度を検出して、混合気を理論空燃比付近に保つようフィードバック制御が行なわれている。

<発明が解決しようとする問題点>

一方、自動車においては低燃費化も要請されており、そのためには通常走行時なるべく酸素過剰の混合気を燃焼させればよいことが知られている。しかしそうすると空燃比がリーン側の酸素過剰空気となって、排気ガス中の有害成分のうち HC, CO は酸化除去できても、 NO_x は触媒床に吸着した O_2 によって活性金属との接触が妨げられるために、還元除去できないという問題があった。そのため従来、触媒によって高

ナゾルの混合物 30~100 部、水 50~100 部の割合で混合するのが好ましく、更には pH 調整剤を添加して pH 3~6 のスラリーとするのが良い。

シリカゾルとアルミナゾルの混合比は、それらの Si / Al 比がゼオライトの Si / Al 比にほど遠くはならない混合比であることが肝要であり、好ましくは両ゾル混合物の Si / Al 比がゼオライトの Si / Al 比の 1/3 ~ 3 倍となるように、シリカゾルとアルミナゾルを混合するのがよい。ゼオライトとしては、 NO_x 分子径よりも僅かに大きい 5~10 Å 程の細孔を有するゼオライトが適当である。

工程(b)において、上記の一体型粗体としては汎用されているセラミック製モノリス、ハニカム型粗体で十分であり、該粗体に上記スラリーを付着させるには、粗体にスラリーを噴射塗布するか成はスラリー中に粗体を浸漬すればよい。焼成は、余分な付着スラリーを圧縮空気又は真空引きにより吹き払ってから、800°C 以下の温

度の排気ガス浄化を図る自動車にあっては混合気を希薄にすることができなかった。

本発明は上記問題点を解決するために為されたものであり、その目的とするところは、リーン側でも NO_x を還元除去でき理論空燃比からリーン側の広い領域にわたって全ての有害成分を十分に除去し得る排気ガス浄化用触媒の製造方法を提供することである。

<問題点を解決するための手段>

本発明の排気ガス浄化用触媒の製造方法は、以下の工程:

- (a) ゼオライト、シリカゾル、アルミナゾル及び水を混合してスラリーを調製する工程、
- (b) 上記スラリーを一体型粗体に付着させ、焼成する工程、
- (c) 触媒用金属の金属塩水溶液に浸漬してゼオライトに触媒用金属をイオン交換する工程からなることを特徴とする。

工程(a)のスラリーを調製する工程においては、ゼオライト 100 部に対し、シリカゾルとアルミ

ナゾルの混合物 30~100 部、水 50~100 部の割合で混合するのが好ましく、更には pH 調整剤を添加して pH 3~6 のスラリーとするのが良い。

工程(c)でイオン交換させる触媒用金属としては、Cu, Cr, Co, Ni, Fe, Mn 等の遷移金属や Pt, Pd, Rh, Ce, Ir, Ru 等の貴金属が挙げられる。イオン交換は上記金属の水溶性塩の水溶液中にゼオライトを浸漬することにより行なうことができる。溶液濃度としては 0.001~0.1 mol/l が適当であり、例えば酢酸銅水溶液の場合、特に 0.02~0.06 mol/l が好ましい(第 2 図参照)。溶液温度は 30±10°C で充分であり、イオン交換時間は 5~140 時間、望ましくは 40~100 時間である(第 1 図参照)。

本発明の製造方法によれば、工程(a)→(b)→(c) の順でも、また工程(c)→(a)→(b) の順でも目的とする触媒を得ることができるが、前者の順によるのがイオン交換効果上好ましい。その理由は、イオン交換される金属は交換容易なサイトからより困難なサイトへと段階的に、例えば第 3 図の構造模式図で示すように A → B → C の順に入り、またサイトは C → B → A と逆順で NO_x 浄化

に有効→無効となる場合を考えれば、最初に全部のゼオライトをイオン交換するよりも第4図に示すように、担体4上のバインダー3間に埋もれたゼオライト粒子2, 2—を除いた表面に現われているゼオライト粒子1, 1—のみをイオン交換したほうが、イオン交換金属5, 5—はNO_xに対しより高活性なサイトまで入る確率が高くなつて触媒活性が向上することになるからである。

<作用>

本発明の製造方法によつて得られる触媒は、その表面が、触媒用金属でイオン交換されたゼオライトで覆われることとなる。ゼオライトはNO_x分子の大きさと並ぶ数Å単位の細孔を有しており、そのため該細孔にNO_xが選択的に取り込まれる。細孔中には上記金属がイオン交換されて活性となつたサイトが存在するため、そこに吸着したNO_xは触媒用金属により還元される。

<実施例>

以下、実施例により本発明を更に詳しく説明

浸透培養機中、70時間室温でイオン交換を行つた。余分な水分を吹き払つた後80°Cで20分間乾燥して排気ガス浄化用触媒Aを製造した。

実施例2, 3

実施例1で用いたゼオライトの代わりに、モルデナイト(Si/A₀比19.0)ならびにフォージャサイト(ゼオライトY; Si/A₀比2.6)を用い、それぞれのSi/A₀比に合わせたバインダーで調製したスラリーを担体にウォッシュコートする以外は実施例1と同様にして、触媒B及びCを製造した。

実施例4～8

実施例1で用いた酢酸銅水溶液の代わりに、種々の金属塩水溶液を用いる外は、実施例1と同様にして、それぞれCo, Ni, Fe, Cr, Mnでイオン交換された触媒D, E, F, G, Hを製造した。各触媒の製造に用いた金属塩は以下の通りである。

する。

実施例1

a) スラリー調製

バインダーとして、Si/A₀比が4.0となるように混合されたシリカゾルとアルミニナルの混合物60部に、ゼオライト(Si/A₀比4.0; 最大細孔径5.9Å)粉末100部及び水60部を加えて充分攪拌し、硝酸アルミニウム溶液でpHを3～6とし、ウォッシュコート用スラリーを調製した。

b) コーティング及び焼成

コーチェライト製モノリス状ニハカム担体を水に浸漬し、余分な水を吹き払つた後、上記a)で得られたスラリーに浸漬し、取出した後余分なスラリーを圧縮空気で吹き払い、80°Cで20分乾燥し、更にこれを600°Cで1時間電気炉中で焼成した。

c) イオン交換

得られた焼成体を酢酸銅[Cu(CH₃COO)₂·H₂O]水溶液(濃度0.04mol/L)を用い、

実施例	触媒	金属塩
4	D 酢酸コバルト	Co(CH ₃ COO) ₂ ·4H ₂ O
5	E 酢酸ニッケル	Ni(CH ₃ COO) ₂ ·4H ₂ O
6	F 塩化第二鉄	FeCl ₂ ·6H ₂ O
7	G 硝酸クロム	Cr(NO ₃) ₃ ·9H ₂ O
8	H 酢酸マンガン	Mn(CH ₃ COO) ₂ ·4H ₂ O

比較例

常法に従い、アーバルミナを担体にウォッシュコートし、焼成後Pt/Rhを担体1g当たり1.5g/0.3g担持した触媒Iを製造した。

試験例1

上記各実施例及び比較例で得られた触媒A～Iを3.0Lエンジンの排気系に取り付け、空燃比(A/F)2.0、入ガス温度600°Cの条件下でのNO_xの浄化率を測定した。その結果を第1表に示す。

第 1 表

実施例名	触媒	基材(Si/A _B 比)	触媒金属	NO _x 净化率
実施例1	A	ゼオライト(40)	Cu	45%
実施例2	B	モルデライト(19)	"	35
実施例3	C	フォージャサイト(26)	"	20
実施例4	D	ゼオライト(40)	Co	30
実施例5	E	"(“)	Ni	35
実施例6	F	"(“)	Fe	25
実施例7	G	"(“)	Cr	25
実施例8	H	"(“)	Mn	20
比較例	I	γ-アルミナ	Pt/Rh	2

実施例9及び試験例2

バインダーのアルミニゾルとシリカゾルの混合比が触媒活性にどのような影響を及ぼすかをみるために、Si/A_B比が0, 50, 100, 200, 400, 1000の6種類のバインダーを用意し、実施例1で使用されたバインダーの代わりに上記6種類のバインダーを用い、またCu塩の代

イトを担体上に付着させたものであるため、リーン空気においてもNO_xが選択的に細孔中の活性サイトに吸着・反応し、浄化される触媒となる。

従って本発明の排気ガス浄化触媒を用いれば、リーン空気走行でも大気中にNO_xを排出する恐れがなくなることから、エンジンの設定空燃比を大きくして、自動車の低燃費化を図ることができる。また混合気を希薄にすることでHC, COの発生自体も低くなる。

またバインダーのSi/A_B比をゼオライトのそれに近くなるようにすると触媒性能が向上するとともに、バインダーとゼオライトとの体積膨張率の差を緩和し耐剥離性に富む触媒となる。

4. 図面の簡単な説明

第1図は、ゼオライト(モルデナイト)のSi/A_B比とのイオン交換時間とイオン交換率の関係を示す図、

第2図は酢酸銅水溶液濃度、pHとイオン交換率の関係を示す図、

わりに貴金属塩を用いる以外は実施例1と同様にして各種の触媒を製造した。それらのA/F=18.0におけるHC, CO, NO_x浄化率を調べた。その結果を第2表に示す。バインダーのSi/A_B比がゼオライトのSi/A_B比40に近い触媒は浄化性能に優れていることが判る。

第2表：浄化率(%)

Si/A _B 比	HC	CO	NO _x
0	80	82	30
50	81	85	60
100	82	85	71
200	76	81	53
400	70	75	15
1000	57	68	1

<発明の効果>

本発明方法により得られる排気ガス浄化用触媒は、触媒能を有する金属でイオン交換されかつNO_x分子の取込みに適する細孔を持つゼオラ

イトを担体上に付着させたものであるため、リーン空気においてもNO_xが選択的に細孔中の活性サイトに吸着・反応し、浄化される触媒となる。

第3図はゼオライトの一例の部分構造を示す模式図、

第4図はゼオライトのイオン交換状態の説明図である。

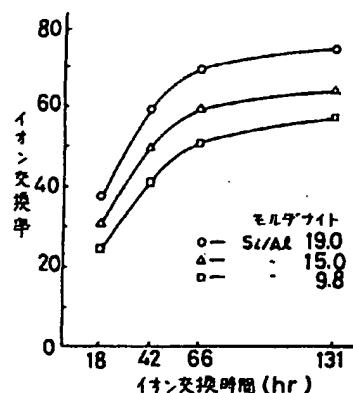
特許出願人 トヨタ自動車株式会社

同 株式会社豊田中央研究所

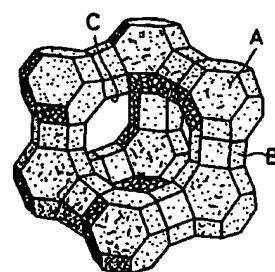
代理人弁理士号 優美ほか2名



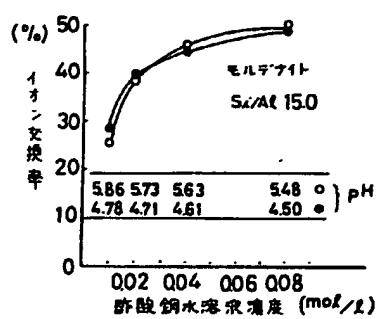
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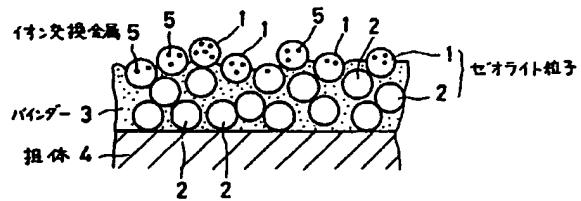
考3図



考2図



考4図



PTO 03-3197

Japanese Kokai Patent Application
No. Hei 1[1989]-135540

MANUFACTURING METHOD FOR AN EXHAUST GAS PURIFYING CATALYST

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UNITED STATES PATENT AND TRADEMARK OFFICE
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MANUFACTURING METHOD FOR AN EXHAUST GAS PURIFYING CATALYST

[Haiki gas jyokayo shokubai no seizo hoho]

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[There are no amendments to this patent.]

Claims

1. A manufacturing method for an exhaust gas purifying catalyst characterized by consisting of the processes below:
 - (a) a process of mixing zeolite, silica sol, alumina sol, and water and preparing a slurry;
 - (b) a process of adhering the aforementioned slurry onto an integrated type catalyst support and firing it;
 - and (c) a process of ion-exchanging the zeolite by a catalytic metal through a soak in a metallic salt aqueous solution of the catalytic metal.

2. The method described in Claim 1 characterized by the mixing ratio between the silica sol and the alumina sol being such that the Si/Al ratio of them is not very different from the Si/Al ratio of the zeolite.

3. The method described in Claim 1 characterized by process (c) being a process that is performed after processes (a) and (b).

Detailed explanation of the invention

Industrial application field

This invention concerns a manufacturing method for an exhaust gas purifying catalyst for vehicles, in particular a catalyst, which can remove NOx at a high ratio even in an excess oxygen atmosphere where the air fuel ratio is on the lean side.

Prior art

As exhaust gas purifying catalysts for cars, catalysts that simultaneously attain an oxidation of carbon monoxide (CO) and hydrocarbons (HC) and a reduction of nitrogen oxides (NOx) have been widely used. With most of such catalysts, a rare metal, such as Pd, Pt, or Rh, for example, and a rare earth metal, such as Ce or La, for example, as a cocatalyst and a base metallic oxide, such as Ni, for example, in some cases are added in an alumina coated layer over a fire resisting catalyst support, as seen in Japanese Kokoku Patent No. Sho 58[1983]-20307, for example.

The purification character of such a catalyst is greatly affected by the set air fuel ratio of the engine. The amount of oxygen (O_2) is in excess after combustion in a thin air mixture, which is on the lean side with a large air fuel ratio, which activates oxidation action and inactivates reduction action. Reversibly, oxidation action becomes inactive and reduction action becomes active on the rich side where the air fuel ratio is small. A catalyst can most effectively function near the theoretical air fuel ratio ($A/F=14.6$) where there is a balance between oxidation and reduction.

Accordingly, with an automobile in which an exhaust gas purifying device that uses a catalyst is attached, the oxygen concentration of the exhaust system is detected, and a feedback control is used so that the air mixture is maintained near the theoretical air fuel ratio.

Problem to be solved by the invention

On the other hand, the attainment of low fuel consumption has also been requested. For the attainment of it, it has been known that an excess oxygen air mixture should be combusted as much as possible generally during traveling. However, there is an issue, wherein when the attained air fuel ratio is an excess oxygen atmosphere on the lean side, HC and CO harmful

components in the exhaust gas can be removed through an oxidation, but NO_x cannot be removed through reduction because contact with an active metal is prevented by O₂, which has been adsorbed into the catalyst bed. As a result, thinning of the air mixture is not conventionally possible in automobiles that attain a high degree of purification of the exhaust gas by a catalyst.

The objective of this invention, which is made for solving the aforementioned problem, is to offer a manufacturing method for an exhaust gas purifying catalyst, which can remove NO_x through reduction even at the lean side and can sufficiently eliminate all harmful components in a large region at the lean side from the theoretical air fuel ratio.

Means for solving the problem

The manufacturing method for an exhaust gas purifying catalyst in this invention has the characteristic of consisting of the processes below:

- (a) a process of mixing zeolite, silica sol, alumina sol, and water and preparing a slurry;
- (b) a process of adhering the aforementioned slurry to an integrated type carrier and firing it;
- and (c) a process of ion-exchanging the zeolite by a catalytic metal through soaking in a metallic salt aqueous solution of the catalytic metal.

In the process of preparing the slurry in process (a), it is ideal to mix at a proportion of 30-100 parts of a mixture of silica sol and alumina sol and 30-100 parts for water for 100 parts of zeolite. Furthermore, the obtainment of a slurry at a pH of 3-6 by adding a pH adjusting agent is desirable.

It is important for the mixing ratio between silica sol and alumina sol to be such that the Si/Al ratio of them is not very different from the Si/Al ratio of the zeolite. It is ideal to mix the silica sol with the alumina sol so that the Si/Al ratio of the mixture is 1/3-3 times the Si/Al ratio of the zeolite.

As the zeolite, zeolite having small holes at a diameter of 5-10Å, which is slightly larger than the diameter of the NO_x molecule, is proper.

In process (b), monolithic and honeycomb type catalyst supports made of ceramic that are widely used are sufficient as the aforementioned integrated type catalyst support. For adhering the aforementioned slurry onto said catalyst support, the slurry may be spray-coated on the support, or the support may be immersed into the slurry. Firing is properly obtained at a temperature below 800°C after blowing away excess attached slurry by compressed air or after vacuum suction.

As catalytic metals for the ion exchange in process (c), transition metals, such as Cu, Cr, Co, Ni, Fe, and Mn, for example, and rare metals, such as Pt, Pd, Rh, Ce, Ir, and Ru, for example, can be listed. The ion exchange can be attained by soaking the zeolite into an aqueous solution of a water-soluble salt of an aforementioned metal. A proper concentration of the

solution is 0.001-0.1 mol/L. For a copper acetate aqueous solution, for example, 0.02-0.06 mol/L is particularly ideal (refer to Figure 2). A sufficient temperature of the solution is 30±10°C. The ion exchange time is 5-140 hours, ideally 40-100 hours (refer to Figure 1).

In the manufacturing method in this invention, the target catalyst can be obtained in the order of processes (a)? (b)? (c) or in the order of processes (c)? (a)? (b), however, the former order is ideal when considering the ion exchange effect because the metal that is ion-exchanged enters gradually from a site where exchange occurs easily to a more difficult site, as indicated by the structural model figure in Figure 3 in the order of A? B? C. While also considering a case, in which sites become valid? invalid for the purification of NOx in the reverse order of C? B? A, the probability for ion exchange metals 5, 5..... to enter a site higher in activity for NOx becomes higher when only ion exchanging the zeolite particles 1, 1.....that appear on the surface except for the zeolite particles 2, 2..... that are buried in the binder (3) over the catalyst support (4), as indicated in Figure 4, than when the entire zeolite is ion-exchanged at first, and the catalytic activity improves.

Operation of the invention

The catalyst that is obtained by the manufacturing method in this invention has its surface covered by zeolite, which is ion-exchanged by a catalytic metal. Zeolite has small holes in the order of several Å, which is equal to the size of the NOx molecule. As a result, NOx is selectively taken into said small holes. Sites in which the aforementioned metal is ion-exchanged and have become active are present in small holes. Therefore, NOx, which has absorbed there, is reduced by the catalytic metal.

Application examples

This invention will be explained in more detail in the application examples below.

Application Example 1

a) Preparation of the slurry

To 60 parts of a mixture of silica sol and alumina sol as a binder, which is mixed together at a Si/Al ratio of 40, 100 parts of a zeolite (Si/Al ratio of 40; maximal small hole diameter of 5.9 Å) powder and 60 parts of water are added, sufficiently stirred, the pH is adjusted to 3-6 with an aluminum nitrate solution, and a wash-coating slurry is prepared.

b) Coating and firing

A cordierite monolithic form honey-comb catalyst support is soaked in water, soaked in the slurry obtained in a) above after blowing away excess water, removed followed by excess

slurry being blown away with compressed air, dried at 80°C for 20 minutes, and furthermore fired in an electric furnace at 600°C for 1 hour.

c) Ion-exchange

The obtained fired product is ion-exchanged using a copper acetate $[Cu(CH_3COO)_2 \cdot H_2O]$ aqueous solution (concentration of 0.04 mol/L) in a penetration culturing machine for 70 hours at room temperature. After blowing away excess water, it is dried at 80°C for 20 minutes, and exhaust gas purifying catalyst A is manufactured.

Application Examples 2 and 3

Catalysts B and C are manufactured in the same manner as Application Example 1 except for using mordenite (Si/Al ratio of 19.0) and aujasite (zeolite Y; Si/Al ratio of 26) instead of the zeolite used in Application Example 1, and wash-coating slurries prepared as binder matching the respective Si/Al ratios, onto the catalyst support.

Application Examples 4-8

Catalysts D, E, F, G, and H that are ion exchanged respectively by Co, Ni, Fe, Cr, and Mn are manufactured in the same manner as Application Example 1 except for using various types of metallic salt aqueous solutions instead of the copper acetate aqueous solution used in Application Example 1. The following metallic salts were used in the manufacture of the catalysts.

実施例	触媒	金 属 塩
① 4	D④ 酢酸コバルト	$Co(CH_3COO)_2 \cdot 4H_2O$
5	E⑤ 酢酸ニッケル	$Ni(CH_3COO)_2 \cdot 4H_2O$
6	F⑥ 塩化第二鉄	$FeCl_2 \cdot 6H_2O$
7	G⑦ 硝酸クロム	$Cr(NO_3)_3 \cdot 9H_2O$
8	H⑧ 酢酸マンガン	$Mn(CH_3COO)_2 \cdot 4H_2O$

- Key:
- 1 Application example
 - 2 Catalyst
 - 3 Metallic salt
 - 4 Cobalt acetate
 - 5 Nickel acetate
 - 6 Ferric chloride
 - 7 Chromium nitrate
 - 8 Manganese acetate

Comparison example

In accordance with a universal method, γ -alumina is wash-coated over a catalyst support, and catalyst I supporting 1.5g/0.3 g of Pt/Rh per 1 l of the catalyst support after firing is manufactured.

Testing example 1

Catalysts A-I obtained in the aforementioned application examples and comparison example are attached to the exhausting system of a 3.0 L engine, and the removal rate for NOx under conditions including an air fuel ratio (A/F) of 20 and a gas entering temperature of 600°C are measured. Table 1 shows the results.

Table 1

Application example No.	Catalysts	Base material (Si/Al ratio)	Catalytic metal	Purification ratio of NOx
Application No. 1	A	Zeolite (40)	Cu	48%
Application No. 2	B	Moldelite (19)	"	55
Application No. 3	C	Forjasite (26)	"	20
Application No. 4	D	Zeolite (40)	Co	30
Application No. 5	E	" ("")	Ni	35
Application No. 6	F	" ("")	Ni	23
Application No. 7	G	" ("")	Cr	25
Application No. 8	H	" ("")	Mn	20
Comparison Example	I	r-alumina	Pt/Rh	2

Application Example 9 and Comparison Example 2

To observe the effect of the mixing ratio between the alumina sol and silica sol in the binder on the catalytic activity, 6 types of binders with Si/Al ratios of 0, 50, 100, 200, 400, and 1000 are prepared. Various types of catalysts are manufactured in the same manner as Application Example 1 except for using the aforementioned 6 types of binders instead of the binder used in Application Example 1 and using a rare metal salt instead of the Cu salt. The HC, CO, and NOx removal rates with an A/F=18.0 are checked. Table 2 shows the results. It can be understood that catalysts having a Si/Al ratio of the binder close to the Si/Al ratio of 40 of the zeolite display an excellent purification performance.

Table 2. Removal Rate (%)

Si/Al ratio	HC	CO	NO _x
0	80	82	30
50	81	85	60
100	82	85	71
200	76	81	33
400	70	75	15
1000	57	68	1

Effect of the invention

The exhaust gas purifying catalyst, which is obtained by the method in this invention, has a zeolite, which is ion-exchanged by a metal having catalytic performance and which also has small holes that are suitable for taking in NO_x molecules, adhered over a catalyst support, and therefore, it can become a catalyst that allows NO_x to selectively adsorb and react at active sites in small holes even in a lean atmosphere and thus purifies.

Accordingly, the risk of exhausting NO_x into the atmosphere during driving in a lean atmosphere is eliminated by using the exhaust gas purifying catalyst in this invention. Therefore, the set air fuel ratio of the engine can be increased, and the attainment of low fuel consumption for a vehicle can be obtained. The generation of HC and CO is also reduced by thinning the air mixture.

The catalytic performance also improves by allowing the Si/Al ratio of the binder to approach that of the zeolite, and a catalyst that is rich in separation resistance is obtained by relieving the difference in the volume expansion ratio between the binder and zeolite.

Brief description of the figures

Figure 1 is a graph showing the relationship between the ion exchange time and the ion exchange rate per the Si/Al ratio of zeolite (mordenite).

Figure 2 is a graph showing the relationship between the concentration of a copper acetate aqueous solution, pH, and the ion exchange rate.

Figure 3 is a model diagram showing a partial structure of an example of zeolite.

Figure 4 is an explanatory diagram of the ion-exchanged state of zeolite.

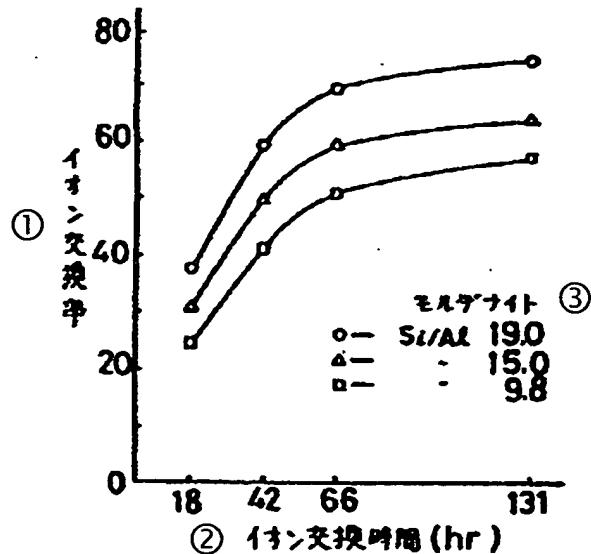


Figure 1

- Keys: 1 Ion exchange rate
2 Ion exchange time (hr)
3 Mordenite

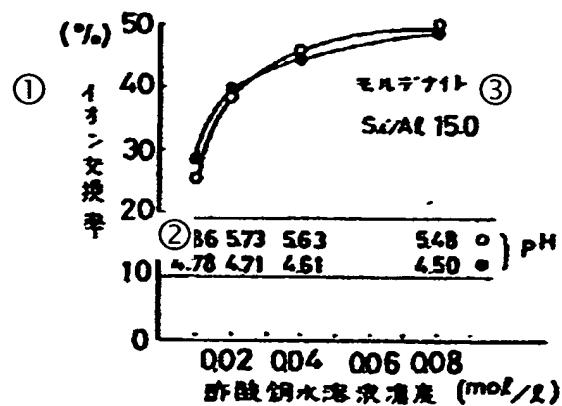


Figure 2

- Keys: 1 Ion exchange rate
2 Concentration of copper acetate aqueous solution (mol/L)
3 Mordenite

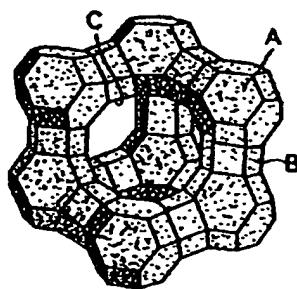


Figure 3

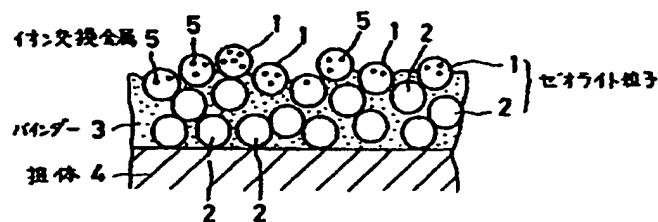


Figure 4

- Keys:
- 1, 2 Zeolite particles
 - 3 Binder
 - 4 Catalyst support
 - 5 Ion exchange metal